

KOKAI PATENT APPLICATION NO. SHO 58-93728

ION-EXCHANGE MEMBRANE

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KOKAI PATENT APPLICATION NO. Sho 58-93728

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ION-EXCHANGE MEMBRANE

[*Ion kohkanmaku*]

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[There are no amendments to this patent.]

Specification

1. Title of the invention

Ion-exchange membrane

2. Claim of the invention

1. A cation exchange membrane characterized by the fact that at least one micron of at least one side of the membrane of a homogeneous perfluorocarbon type cation exchange membrane produced by extrusion molding method is removed.

2. A cation exchange membrane used for electrolysis of an alkali metal salt wherein the ion-exchange membrane described in Claim 1 of the invention has the exchange capacity of 0.5 to 2.0 milliequivalents per gram of dry film (H type).

3. A cation exchange membrane wherein the ion-exchange membrane described in Claim 1 of the invention is one or both of sulfonic acid group or carboxylic acid group.

4. A cation exchange membrane wherein the sulfonic acid group or carboxylic acid group exists laminarly in the cation exchange membrane described in claim 3 of the invention.

3. Detailed description of the invention

The present invention pertains to a cation exchange membrane characterized by the fact that at least one micron of at least one side of the membrane of a homogeneous perfluorocarbon type cation exchange membrane produced by extrusion molding method is removed.

Ion-exchange membranes are used for a variety of industrial purposes such as electroanalysis, diffusion analysis, diaphragm for reverse osmosis of electrolyte reaction and ultrafiltration. In particular, rapid technical development is observed in electrolysis of salt with an ion-exchange membrane used industrially in recent years. Initially, the target was production of a high concentration caustic soda at a high current efficiency with a perfluorocarbon type ion-exchange membrane, but currently, the current efficiency is at least 90%, and maintenance of the above-mentioned level for an extended time is made possible. Thus, the major challenge in these days is reduction in the electrolytic voltage. Analysis of the electrolytic voltage shows a high proportion of the voltage decrease based on theoretical decomposition voltage, cathodic over-voltage, and electrical resistance of the film. Among those listed above, nothing can be done about the theoretical decomposition voltage, but for the cathodic over-voltage, development of active cathodes has been pursued and has contributed to a reduction in the decomposition voltage.

[p. 2]

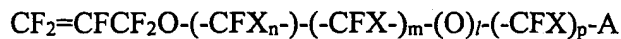
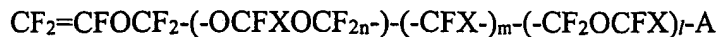
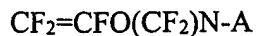
Furthermore, as a means for reduction of the electrical resistance of the film, change in the composition of the ion-exchange membrane, and selection of the mesh, cloth, etc. for reinforcement is done in an effort to reduce the electrical resistance of the film. Furthermore, a reduction in the thickness of the film is one effective method, but limitation is placed on correlation with the amount of salt included in the caustic soda produced, and it is necessary to take the mechanical strength of the film into consideration.

Furthermore, non-uniformity in the film cross-section of the film structure of the extrusion molded ion-exchange membrane is made known, and the present inventors found that to their surprise, an ion-exchange membrane with a low electrical resistance for electrolysis can be produced when the surface layer of the perfluorocarbon type ion-exchange membrane produced by extrusion molding method is removed. In the past, it is known that a sharp reduction in the electrical resistance can be achieved when mixing of a fine powder of hydrocarbon type ion-exchange resin and an inert polymer is carried out and a heterogeneous ion-exchange membrane is formed and when the surface layer is removed with sand paper, etc. and the fine particles of the ion-exchange resin are exposed since the surface layer of the film is covered with an inert polymer, and the electrical resistance is high. Furthermore, presence of a high-density thin layer referred to as a skin layer on the film surface is known in reverse osmosis films. In general, in a polymer film, in particular, in an extrusion molded film, structural differences exists inside the film and on the surface layer. However, the effect on the above-mentioned electrical resistance and other electrochemical properties in the surface layer of the homogeneous ion-exchange membrane has not been studied. A test was done on the premise of the presence of non-uniformities in the extruded molded film structure in an ion-exchange

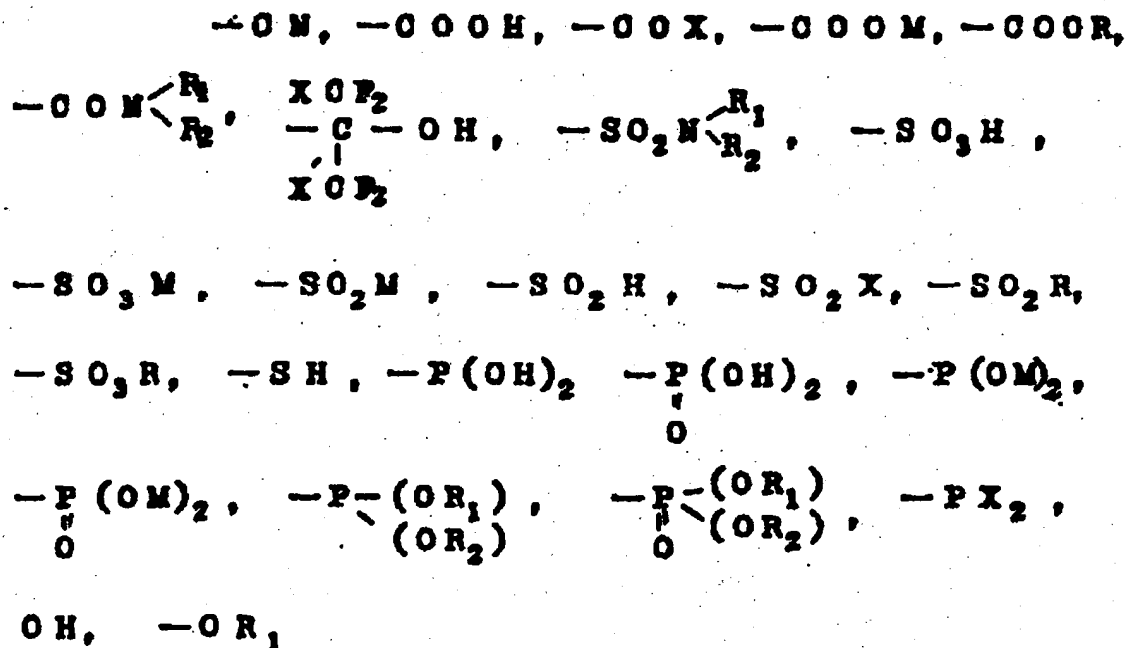
membrane and that these had an effect on the electrical resistance of the film, and the present invention was accomplished.

The heterogeneous cation exchange membrane discussed in the present invention is different from a cation exchange membrane structure consisting of an inert thermoplastic polymer material for retention of an insoluble cationic exchange resin known as a conventional heterogeneous film. An inert polymer having a cation exchange group suitable for extrusion molding for reinforcement of the perfluorocarbon type polymer, for example, fibrillated polytetrafluoroethylene, is included, the material belongs to the homogeneous cation exchange membrane of the present invention. In other words, a homogeneous ion-exchange membrane includes non-uniformity in the distribution of the ion-exchange group from the standpoint of micro-structure, but all perfluorocarbon-type polymer compounds having an ion-exchange group or easily introduced with an ion-exchange group can be formed into a film and can be used as a cation exchange membrane after an ion-exchange group induction process is included.

As a perfluorocarbon type cation exchange membrane produced by the extrusion molding method of the present invention, a perfluorosulfonic acid type membrane produced by an hydrolysis reaction for a perfluorocarbon type ion-exchange membrane cation exchange membrane produced by extrusion molding of tetrafluoroethylene and perfluoro(3,6-dioxo-4-methyl-7-octene sulfonyl fluoride), etc. can be mentioned. In general, it is not especially limited as long as the perfluorocarbon type cation exchange membrane shown in the following general formula is used. For the cation exchange group, a sulfonic acid group, carboxylic acid group, phosphoric acid group, phosphorous acid group, tertiary alcohol group, sulfonic acid amide, etc. can be used. And examples are shown below. Cation exchange groups such as



(Wherein, X, X' and X'' are -F, -CF₃ and -C₂F₅. n, m, l and p are either 0 or integers of up to 12, and A is

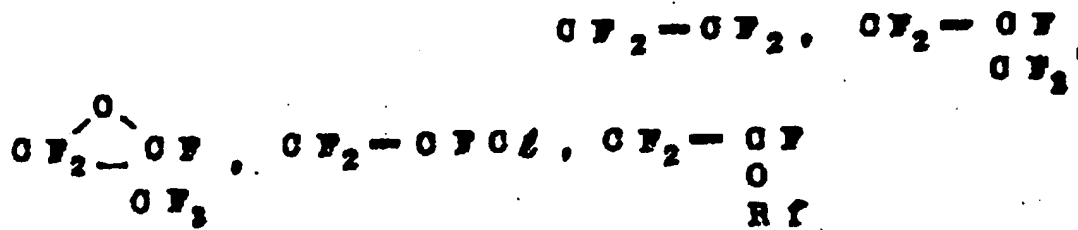


etc. In this case, X and X' are halogens,

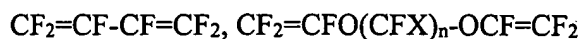
[p. 3]

M is an alkali metal, alkaline earth metal, R₁ is an alkyl group with C₁~C₁₂, R₂ is an alkyl group with C₁~C₁₂ or hydrogen atom, etc.) or copolymers produced by copolymerization of a vinyl monomer having a functional group that can be easily converted to a cation exchange group and

fluorolefins, for example,



(Refining is a saturated perfluoroalkyl group)



(X is F-CF₂)

etc. and formed into a film, can be mentioned. The above-mentioned films are cation exchange membranes capable of producing an alkali metal hydroxide at a high concentration at a high current efficiency upon introduction of an ion exchange group after the film formation, as needed, and in some cases, it is necessary to form a two-layer film where a dissimilar cation exchange group or dissimilar layers having a different density of exchange groups for further increase in the current efficiency.

Especially, in order to maintain high current efficiency and to maintain a lower electrical resistance of the film, for example, a film having sulfonic acid groups on the anodic side and carboxylic acid groups on the cathodic side can be mentioned. Furthermore, a film where the exchange capacity on the film surface on the anodic side is increased and the cathodic side is

decreased, and an ion-exchange membrane where a sulfonic acid group is used for the anode side and a thin layer bonded with a phosphoric acid group, tertiary alcohol group, and a sulfonic acid amide having a detachable hydrogen atom for the cathode side, etc. can be mentioned.

In addition, a method where the current efficiency of the cation-exchange membrane used for hydrolysis is increased through a chemically treated cation-exchange membrane, for example, a hydrolysis conversion reaction of the sulfonic acid group, conversion of the sulfonic acid group to a carboxylic acid group, conversion of the carboxylic acid group to a sulfonic acid group, an induction reaction of the sulfonic acid amide, etc., is known as well. In the present invention, the type of the film used not especially limited as long as a perfluorocarbon type ion-exchange membrane where extrusion molding is used at some time during the course of production, and a laminated film or a film having a cloth backing can be used effectively.

Extrusion molding of a film is achieved by melting a perfluorocarbon type polymer compound (molecular weight of at least 10000) containing an acid halide group, acid anhydride group, acid ester group, etc. used as the precursor of the cation-exchange membrane using an inflation molding method or T-die molding method. In general, the thickness of the film used for the ion-exchange membrane is in the range of 10 microns to 800 microns and in the range of 20 microns to 250 microns is further desirable.

Furthermore, as a method used for removal of at least 1 micron from one side of the surface layer of the above-mentioned homogeneous ion-exchange membrane, any known industrial method can be used in this case, as well. In other words, removal based on chemical reaction or physical method can be used in this case. In general, perfluorocarbon type compounds have high chemical resistance are stable and physical removal is easy, and for

chemical removal, sodium, naphthalene, n-butyl lithium, alkali metals, alkali metal amalgams, etc. can be used and defluorination can be easily achieved. Furthermore, it is known that rupturing and decomposition of the ether bond can be easily achieved for perfluoro compounds having an ether bond with aluminum chloride or aluminum bromide. Therefore, a surface treatment is carried out for the surface layer of a cation-exchange membrane or precursor thereof with an organic or inorganic reagent capable of decomposing the above-mentioned perfluorocarbon type polymer compound and removal of at least 1 micron of the surface layer is carried out. In other words, a method wherein a defluorination reaction is carried out and oxidation decomposition is performed, a method wherein rupturing of the polymer principle chain or side chain of the surface layer of the perfluorocarbon type polymer is carried out and elution and decomposition is performed in a concentrated caustic alkali, a method wherein decomposition of the surface layer of the perfluorocarbon type polymer compound is carried out for a cation-exchange membrane or precursor thereof by means of a chemical reaction, etc. can be used without any problem.

[p. 4]

As for physical methods, a method where the surface of the above-mentioned perfluorocarbon type ion-exchange membrane is sliced off with a sharp blade, where, for example, a sharp blade is fastened at a specific distance from a rotating roll while the film is placed on the rotating roll and removal the surface layer of the said polymer film to a specific thickness can be mentioned as a suitable method for continuous removal of a constant thickness. Furthermore, in the case of a relatively small area, a sand blasting method, polishing with sand paper, etc. can be mentioned. In addition, sputtering method, flame method, etc. can be used

effectively, as well. Upon removal of the surface layer of the film using a physical or chemical means, the thickness of the area removed is at least 1 micron. The thickness and density of the surface of the film varies significantly depending on the production condition and composition of the perfluorocarbon type polymer membrane material, and composition of the polymer material, etc., and in some cases, removal of 100 angstroms is adequate, but in general, removal of at least 1 micron is required, and more than 1 micron can be removed without any problem. The thickness of removal is selected according to the thickness of the cation-exchange membrane. For example, in the case of a cation-exchange membrane having a thickness of 150 microns, the effect on the film thickness is low when removal to 10 microns is carried out, and an increase in the salt content in the caustic soda generated is insignificant but when 50 microns is removed from a film thickness of 100 microns, an increase in the salt content in the caustic soda generated cannot be ignored. Therefore, the thickness of removal of the surface layer varies depending on the application, and a significant reduction in the electrical resistance can be observed when at least 1 micron of the surface layer is removed. Furthermore, removal of 1/3 of the total film thickness leads to a reduction in the film strength and increase in the salt content.

It is not known the reason why removal of the surface layer of the cation-exchange membrane results in a reduction in the electrical resistance of the film, but it is hypothesized that, as in the case of the high-density membrane referred to as a skin layer that exists on the film surface member of reverse osmosis films, a difference in the polymer structure based on the affinity between the slit material and the polymer or a difference in the orientability of the polymer in the area that comes in contact with slit material is produced on the surface of the perfluorocarbon type ion-exchange membrane at the time of extrusion molding, and a difference

in the surface layer member of the film versus the interior of the film is generated. And it is further hypothesized that a difference in crystallinity of the polymer results due to differences in the cooling at the surface layer versus the inside polymer layer when the polymer is extruded from the slit as a film. In either case, according to the tests conducted, the area mainly subjected to the above-mentioned influence is the region up to 1 micron below the surface of the film. It seems that the above-mentioned film surface layer member forms a kind of barrier when ions enter the film or are released into the solution from inside the film. Therefore, upon removal of the above-mentioned barrier layer, the electrical resistance of the film can be reduced significantly. Furthermore, it is desirable when removal is carried out for both surfaces of the cation-exchange membrane, rather than one surface. When one surface alone is removed, a higher effect can be achieved when the side where the ion enters the film is removed.

Furthermore, upon removal of the film surface layer member, 1) a method where a precursor without the cation exchange group is not introduced is removed and a cation exchange group is introduced, 2) a method where a cation exchange group is introduced and subsequently removed, 3) a method where removal is done before treatments such as with a weak acid cation exchange group is done in order to increase current efficiency, 4) a method where removal is done after treatments such as with a weak acid cation exchange group in order to increase current efficiency, etc. can be mentioned, and among those listed above, methods 2) and 3) are especially desirable. In particular, in an electrolysis reaction of an alkali metal salt, in order to maintain high current efficiency at the time of formation of caustic soda, a membrane of a cation exchange group of a weak acid is formed in many cases and a thickness of the above-mentioned film with several microns is adequate.

A layer produced by performing an oxidation reaction, reduction reaction, or bonding a thin film having a weak acid cation exchange group with a strong acid cation-exchange membrane is destroyed in some cases. Thus, in the case when the thin layer of the above-mentioned weak acid cation exchange group is formed using a chemical reaction, removal of the surface layer of the film should be carried out before the above-mentioned chemical reaction.

[p. 5]

In the following, the content of the present invention is explained further in specific terms with application examples, but the present invention is not limited in any way to these application examples.

Application Example 1

An hydrolysis reaction was carried out for a copolymer sheet made of tetrafluoroethylene and perfluoro(3,6-dioxo-4-methyl-7-octene sulfonyl fluoride) and extruded from a T-die so as to produce film with an exchange capacity of 0.91 milliequivalents per gram of dry film (H type) and a thickness of 178 microns (referred to as film A). A sharp blade was applied to both film surfaces of the above-mentioned film and removal of the surface film to a depth of 5 microns from each side was carried out. The thickness of the film was 168 microns when measured by a micrometer (referred to as film B). Furthermore, removal was carried out for approximately 10 microns of one surface of film A alone, in the same manner (referred to as film C). Furthermore, according to the method described in the specification of Japanese Kokai [Unexamined] Patent Application No. Sho 53-58493 [1978], sulfonyl chlorination was carried out for the sulfonic acid

in a phosphor pentachloride and conversion of the sulfonyl chloride into a carboxylic acid group based on aerial oxidation in an alcohol was carried out for film A; then, an hydrolysis reaction was carried out for the residual sulfonyl chloride to form a sodium sulfonate, and formed into a double-structured ion-exchange membrane where a carboxyl group is included as the ion exchange group in the surface layer and a sulfonic acid group is included as the ion-exchange group in the inner layer was produced (referred to as film D).

Furthermore, the above-mentioned treatment was carried out for the aforementioned film B and production of an ion-exchange membrane was carried out (referred to as film E).

And furthermore, the above-mentioned treatment was carried out for the aforementioned film C and production of an ion-exchange membrane was carried out (referred to as film F). Furthermore, the above-mentioned treatment was carried out for the smooth surface of film C so as to produce film G.

Using the above-mentioned films produced, an electrolysis was carried out for a salt solution. In other words, an electrolytic bath with an effective energizing area of 1 dm^2 , and having a ruthenium oxide coating on titanium of anode and soft iron of cathode, at a current density of 30 A/dm^2 , at a temperature of 80°C , salt concentration in the anodic chamber of 3.5N and 9N of caustic soda of 9N was retrieved from the anodic chamber. In each film, the current efficiency was approximately 95%, and the amount of salt in the caustic soda was approximately 60 ppm (in terms of 50% in terms of caustic soda). The electrical resistance and electrolytic voltage of the films are shown in Table I.

Table I

	Electrical resistance (ohm-cm ²)	Film thickness (microns)	Specific resistivity (ohm-cm)	Electrolytic voltage (V)
Sulfonic acid type film				
Before removal (film A)	0.56	178	31.5	--
Removal of 5 microns from each surfaces (film B)	0.42	168	25.0	--
Removal of 10 microns from one surface (film C)	0.49	168	29.2	--
Carboxylic acid layer formation film				
Carboxylation of film A (film D)	1.04	178	59	3.28
Carboxylation of film B (film E)	0.85	168	51	3.03
Carboxylation of the sliced surface of film C (film F)	0.92	168	55	3.20
Carboxylation of non-sliced surface of film C (film G)	0.88	168	52	3.13

Application Example 2

An extrusion molding was performed for a copolymer of tetrafluoroethylene and $\text{CF}_2=\text{CF}-\text{O}-(\text{CF}_2)_3-\text{COOCH}_3$ to form a film with a thickness of 170 microns.

The exchange capacity of the film was 1.45 milliequivalents/ gram of dry film. The film was then immersed in a mixed solution of 10% water-methanol (1:1) for 16 hours at 50°C so as to produce a cation-exchange membrane having a carboxylic acid group. For the film produced, approximately 5 microns was removed from each side for the anodic side and the cathodic side by [rubbing with] sand paper (product of Nagatsuka Co., Ltd., AA400), and production of three different types of film was carried out. Measurement of the thickness of the film was done with a micrometer. For the films produced above, examination of the electrochemical properties was carried out and electrolysis was performed. The results obtained are shown in the Table II below.

In this case, 35% caustic soda was retrieved from the cathodic chamber steadily, and the

rests are the same as in the case of application example 1.

Table II

	Electrical resistance (ohm-cm ²)	Film thickness (microns)	Specific resistivity (ohm-cm)	Electrolytic voltage (V)
Film before the surface removal treatment	1.52	170	89.4	3.32
Film after the surface removal treatment (both surfaces)	1.29	160	80.6	2.95
(Anodic side)	1.32	160		3.05
(Cathodic side)	1.40	160		3.25

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Application Example 3

Copolymerization reaction was performed for tetrafluoroethylene and $\text{CF}_2=\text{CFC}-(\text{CF}_2)_4-\text{SO}_2\text{F}$ with an azobisisobutyronitrile as a catalyst and production of a polymer was performed. Subsequently, extrusion molding was performed to produce a film with a thickness of 150 microns. The film was then dipped in a hydrolytic bath of dimethyl sulfoxide, water and potassium hydroxide (600:400:15) and the sulfonyl fluoride group was converted to a sulfonic acid group. The above-mentioned conversion capacity was 1.01 milliequivalents/gram of dry film (H type). A steam of phosphorus pentachloride was brought into contact with one surface of the aforementioned cation-exchange membrane and the sulfonic acid group was converted to a sulfonyl chloride group, and aerial oxidation was carried out in n-butyl alcohol, then the film was dipped in the above-mentioned hydrolytic bath for a second time so as to produce a film having a carboxylic acid of approximately 10 microns on one surface.

The surface layer at the anodic side and cathodic side of the above-mentioned film produced was polished by sand paper (product of Sankyo Rika Co., Ltd., CC600CW) and approximately 5 microns of the surface layer was removed. Properties of the above-mentioned

films and electrolysis performance are shown in Table III. In this case, 35% caustic soda was steadily retrieved from the cathodic chamber.

Table II

	Electrical resistance (ohm-cm ²)	Film thickness (microns)	Specific resistivity (ohm-cm)	Electrolytic voltage (V)	Current efficiency (%)
Film before surface removal treatment	1.1	150	73	3.30	96
Film after removal of the anodic side	0.90	140	64	3.15	96
Film after removal of the cathodic side	0.95	140	68	3.21	92
Film after both surface removal treatment	0.85	140	61	3.00	95

Application Example 4

20 microns of one surface of a sheet (before hydrolysis reaction treatment) made of a copolymer of tetrafluoroethylene and perfluoro(3,6-dioxo-4-methyl-7-octene sulfonyl fluoride) used in application example 1 as explained above. Subsequently, the sheet was dipped in methanol containing 10% NaOH for 10 hours at room temperature and a hydrolysis reaction was carried out for the sulfonyl fluoride group in the sheet and it was converted to sodium sulfonate. The sheet was then immersed in 1N hydrochloric acid for 15 hours to convert into an H acid type. Subsequently, a water wash was carried out and vacuum drying was further carried out to produce an acid type sheet.

Furthermore, in order to convert the sulfonic acid group into a carboxylic acid group, the acid type sheet was arranged inside the wall of the cylindrical glass reactor (inner diameter of 10 cm) with the sliced surface facing outward, and a disinfectant lamp made by Toshiba Corp. (GL-15) was placed at the center area of the reactor so as to form equal distances from the surface of

the sheet. The aforementioned reactor was immersed in an oil bath and heating was done to 150°C. Thorough purging of the reactor was done with nitrogen, and exhausting was done with a vacuum pump. Subsequently, 1 kg/cm² of nitrogen monoxide was fed from a bomb, the reactor was sealed, the disinfectant lamp was turned on, and radiation was carried out for 30 minutes. Subsequently, the lamp was turned off and nitrogen was introduced to the reactor, and purging of the nitrogen monoxide was carried out.

For comparison, the same treatment was carried out for a sheet from which one surface was not removed. When measurement was carried out for the infrared spectral (A.T.R method) for the sheet after the treatment, absorption of the carboxylic acid group was observed at 1780 cm⁻¹ in the area where the light was applied, and an absorption band of the sulfonic acid group at 1060 cm⁻¹ was hardly observed. On the other hand, absorption at 1780 cm⁻¹ was not recognized on the opposite side in each case and intense absorption at 1060 cm⁻¹ was recognized.

In order to use the above-mentioned sheets for electrolysis of cation-exchange membrane, the sheet after the treatment was dipped in methanol containing 10% NaOH at room temperature for 2 hours. After dipping, a water wash was carried out and electrolysis was performed for the salt water according to the method described in Application Example 1. The results obtained are shown in Table IV. In this case, upon arranging the sheet in the hydrolytic bath, the surface containing the carboxylic acid groups (irradiated surface) was placed toward the cathodic side.

Table IV

	Electrolytic voltage (V)	Current efficiency
Film with removed surface	3.18	95
Film without removed surface	3.25	95

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WPI Acc No: 1983-708272/ 198328

Cation exchange membrane with ion electric resistance - obtd. by removing surface layer from homogeneous per-fluorocarbon cation exchange membrane

Patent Assignee: TOKUYAMA SODA KK (TOKU)

Number of Countries: 001 Number of Patents: 002

Patent Family:

Patent No	Kind	Date	Applicat No	Kind	Date	Week
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JP 58093728	A	19830603	JP 81191822	A	19811201	198328 B
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JP 89000977	B	19890110			198905	
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Priority Applications (No Type Date): JP 81191822 A 19811201

Patent Details:

Patent No	Kind	Lan Pg	Main IPC	Filing Notes
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JP 58093728	A	6		
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Abstract (Basic): JP 58093728 A

Cation exchange membrane is formed by removing at least 1 micron thick surface layer from a homogeneous perfluorocarbon type cation exchange membrane (I) produced by extrusion-moulding. The membrane shows reduced electric resistance.

Pref. (I) is e.g. perfluorosulphonic acid type membrane obtd. by hydrolysing perfluorocarbon type cation exchange membrane obtd. by extrusion-moulding copolymer of TFE and perfluoro(3,6-dioxo-4-methyl 7-octenesulphonyl)fluoride). (I) is 10-800, (50-250) microns thick. At least 1 micron thick surface layer is removed from (I) using (in)organic reagents decomposing perfluorocarbon type high molecular cpds., e.g. sodium, naphthalene aluminium chloride, aluminium bromide, or by cutting the surface of (I) using a sharp knife. The membrane is conveyed on the rotary roll and the surface of the membrane is cut away with the knife.

⑨ 日本国特許庁 (JP)

⑪ 特許出願公開

⑫ 公開特許公報 (A)

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C 08 J 5/22
C 25 B 13/08
// B 01 J 47/12

識別記号
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庁内整理番号
7415—4F
6761—4K
7918—4G

⑬ 公開 昭和58年(1983)6月3日

発明の数 1
審査請求 未請求

(全 6 頁)

⑭ イオン交換膜

徳山市御影町1番1号徳山曹達
株式会社内

⑮ 特 願 昭56—191822

⑯ 発 明 者 武末正宏

⑰ 出 願 昭56(1981)12月1日

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⑳ 発 明 者 中原昭彦

明 細 書

1. 発明の名称 イオン交換膜

2. 特許請求の範囲

1. 押し出し成型によって作られた均質なパーフルオロカーボン系陽イオン交換膜の少なくとも一方の膜面を少なくとも1ミクロン除去した陽イオン交換膜。
2. 特許請求範囲第1項記載のイオン交換膜が0.5乃至2.0ミリ当量1グラム乾燥膜(H型)の交換容量を有しているアルカリ金属塩電解用陽イオン交換膜
3. 特許請求範囲第1項記載のイオン交換膜の交換基が、スルホン酸基及びカルボン酸基のいずれか又は両方である陽イオン交換膜。
4. 特許請求範囲第3項記載の陽イオン交換膜に於いて、スルホン酸基とカルボン酸基が層状に存在する陽イオン交換膜。

3. 発明の詳細な説明

本発明は押し出し成型によって作られた均質なパーフルオロカーボン系陽イオン交換膜の、

少なくとも一方の膜面を少なくとも1ミクロン除去したアルカリ金属塩電解用イオン交換膜に係る。

イオン交換膜は電気透析、拡散透析、電解反応の副膜逆浸透、限外ろ過と各種の分野で工業的に利用されている。特に近年工業化されているイオン交換膜法食塩電解は省エネルギープロセスとして、その技術的な進歩はめざましいものがある。当初、パーフルオロカーボン系イオン交換膜で高濃度苛性ソーダを高い電流効率で取得することをめざしていたものが、現在電流効率は90%以上となり、それを長期間に亘って維持することが可能となった。このため、現在における最大の課題は電解電圧をより低くすることである。電解電圧を解析すると理論分解電圧、陰極過電圧、膜の電気抵抗による電圧降下等が大きな割合を占めている。このうち理論分解電圧は如何ともし難いものであるが、陰極過電圧については活性な陰極が開発され電解電圧の低減に寄与している。また膜の電気抵抗を低

(1)

(2)

減する方法として、イオン交換膜の組成を変えること、補強用の網、布等を選択することなどが、膜の電気抵抗の低減手段として試みられている。また、膜の厚みを薄くすることも一つの有効な方法であるが、生成苛性ソーダ中の食塩含量との相関で限界があるし、膜の機械的強度も配慮しなければならない。

我々は上記の種々の試み以外に、押し出し成型されたイオン交換膜の膜構造の膜断面についての不均質性があることを知り、押し出し成型で作られたパーフルオロカーボン系イオン交換膜の表層部を薄層状に削除することによって意外に電気抵抗の低い電解用イオン交換膜を得ることを見出した。従来から炭化水素系の微粉状イオン交換樹脂と不活性な高分子を混合してフィルムとする所謂不均質イオン交換膜で、膜表層部が不活性な高分子で覆われているために膜の電気抵抗が高く、これの表層部をサンドペーパー等で削除すると、イオン交換樹脂の微粒子が露出し、電気抵抗が著しく低下することは知ら

(3)

れている。また、逆浸透膜に於いては膜表層部にスキン層と称する緻密な薄層が存在することが知られている。一般に高分子フィルム、特に押し出し成型されたフィルムに於いてはフィルム内部と表層部で構造的な違いがあることは知られるところである。しかし、現在まで所謂均質なイオン交換膜の表層部にこのような膜の電気抵抗その他の電気化学的性質に影響を及ぼす効果については検討されていなかった。我々は押し出し成型フィルムの膜構造の不均一性が、イオン交換膜に於いても存在し、これが膜の電気抵抗に何らかの作用をするものと想定して実験を行い、本発明を完成させるに至った。

本発明でいう均質な陽イオン交換膜とは従来の不均質膜として知られている不溶不融の陽イオン交換樹脂を膜状に保持するために、不活性な熱可塑性高分子体から構成された陽イオン交換膜に対していうものである。押し出し成型可能な陽イオン交換基を有する、或いは陽イオン交換基の導入可能なパーフルオロカーボン系高

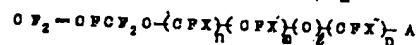
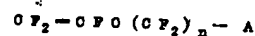
(4)

分子に補強のための不融な不活性な高分子、例えばフィブリル化したポリテトラフルオロエチレンが共存しているものも、本発明の均質陽イオン交換膜の部類に属する。換言すれば、均質イオン交換膜とはミクロ構造で見ればどのようなイオン交換膜にもイオン交換基の分布に不均一性が存在するものであるが、イオン交換基を有する或いは容易にイオン交換基を導入出来るパーフルオロカーボン系高分子化合物が、それ単体でも成膜でき、イオン交換基導入工程を経て後、陽イオン交換膜として使用することが出来るものは全て含まれるのである。

本発明の押し出し成型によって作られたパーフルオロカーボン系陽イオン交換膜には、良く知られているものとしてテトラフルオロエチレンとパーフルオロ(3,6-ジオキサ-4-メチル-7-オクテンスルホンフルオリド)の共重合体を押し出し成型したパーフルオロカーボン系陽イオン交換膜を加水分解したパーフルオロスルホン酸型の膜等がある。一般に次式で

(5)

示されるパーフルオロカーボン系の陽イオン交換膜であれば特に限定されない。陽イオン交換基としてはスルホン酸基、カルボン酸基、リン酸基、亜リン酸基、第三級のアアルコール基、スルホン酸アミド基などが適宜用いられる。これらを例示すると



(X, X', X''はそれぞれ $-\text{F}$, $-\text{CF}_3$, $-\text{O}_2\text{F}_3$ を示す。n, m, l, pは0または12までの正の整数。Aは $-\text{OH}$, $-\text{COOH}$, $-\text{O}_2\text{X}$, $-\text{COOM}$, $-\text{COOR}$, $-\text{O}_2\text{N} \begin{smallmatrix} \text{R}_1 \\ \text{R}_2 \end{smallmatrix}$, $\begin{smallmatrix} \text{XOCF}_2 \\ \text{C} \\ \text{XOCF}_2 \end{smallmatrix} -\text{OH}$, $-\text{SO}_2\text{N} \begin{smallmatrix} \text{R}_1 \\ \text{R}_2 \end{smallmatrix}$, $-\text{SO}_3\text{H}$, $-\text{SO}_3\text{M}$, $-\text{SO}_2\text{M}$, $-\text{SO}_2\text{H}$, $-\text{SO}_2\text{X}$, $-\text{SO}_2\text{R}$, $-\text{SO}_2\text{R}$, $-\text{SH}$, $-\text{P}(\text{OH})_2$, $-\text{P}(\text{OH})_2$, $-\text{P}(\text{OM})_2$, $-\text{P}(\text{OM})_2$, $-\text{P} \begin{smallmatrix} \text{OR}_1 \\ \text{OR}_2 \end{smallmatrix}$, $-\text{P} \begin{smallmatrix} \text{OR}_1 \\ \text{OR}_2 \end{smallmatrix}$, $-\text{PX}_2$, OH , $-\text{OR}_1$ 等を示す。但し、X, X'はハロゲン、

(6)

層状に切削する方法、例えば回転ロール上を膜を走らせながら、回転ロールから一定の距離のところに鋭利な刃物を固定してロール上を膜を移動しながら、一定の厚みに薄膜状に高分子膜状物の表層部を切削除去する方法が連続的に一定の厚みに表層部の薄層を除去する方法としては有効である。その他、比較的小面積のものに実施する場合には、サンドブラストをかける方法、サンドペーパーで研磨除去する方法など有効である。その他スパッタリング、火炎処理等適宜実施することができる。膜表層部を物理的・化学的手段によって除去する際、その除去する厚みは少なくとも1ミクロン必要である。パーフルオロカーボン系高分子膜状物の製造条件及び組成、高分子物質の組成等によって膜表面のうち密層の厚み、密度は著しく異なり、或る場合には100Å程度の削除によっても有効な場合があるが、一般的には少なくとも1ミクロン削除すれば有効であり、1ミクロン以上削除しても何ら差しつかえない。イオン交換膜の厚みに

(11)

応じて削除する厚みは選択すればよい。例えば150ミクロンの厚みを有する陽イオン交換膜の場合、10ミクロン削除しても膜厚に対する影響は少なく、従って生成苛性ソーダ中の食塩含量の増大は無視しうる程度であるが、100ミクロンの厚みの膜を50ミクロン削除した場合には、生成苛性ソーダ中の食塩含量は無視し得なくなるまで増大する。従って表層部を削除する厚みは、それを適用する対象に応じて選択しなければならないが、少なくとも1ミクロン以上削除すればイオン交換膜の電気抵抗は顯著に低下する。また膜厚の $1/3$ 以上削除するのは無意味であるばかりか、膜強度の低下や食塩の混入量の増大を来し、好ましくない。

さて、このように陽イオン交換膜の表層部を削りて膜か削除したのみで膜の電気抵抗が低減する理由については明らかでないが、逆浸透膜に於いて膜表層部にスキン層という非常に密な薄層が存在するように、押し出し成型時にパーフルオロカーボン系陽イオン交換膜の表面に、ダイ

(12)

スのスリットから押し出される際、スリット材質とポリマーの親和性に基づく高分子構造の違い或いはスリット材質と接触する部分でのポリマーの配向性の違いが生じ、これが膜表層部と膜内部の違いを引き起こすものと推測される。また、ポリマーがスリットからフィルムとして押し出されたとき、冷却のされ方が表層部と内部で異なり、ポリマーの結晶性の違いとして発現しているとも推測される。いずれにせよ、これらの影響を強く受ける部分は、フィルム表面より1ミクロン以下の部分であることがモデル実験により確かめられた。この膜表層部分は、イオンが膜内に入るとき、また膜内から溶液中に出るとき、一層のバリアーとなっているものと思われる。従ってこのようなバリアー層を除去することによって、膜の電気抵抗が著しく低減するものと思われる。また陽イオン交換膜の一方の膜面を除去するよりは両面を除去することが望ましい。一方の面だけ除去する場合はイオンが膜内に入る側を除去した場合が効果は大

(13)

きい。

また、膜表層部を削除するとき、1)陽イオン交換基の導入されていない前駆体を削除して陽イオン交換基を導入する方法、2)陽イオン交換基を導入後削除する方法、3)電流効率向上のための弱酸性陽イオン交換基を導入等の処理前に削除する方法、4)電流効率向上のための弱酸性陽イオン交換基等を導入後に削除する方法等、いずれの場合も有効であるが、最も好ましいのは2)及び3)である。特にアルカリ金属塩電解にあっては、高い苛性ソーダ取得時の高電流効率を維持するために、弱酸性の陽イオン交換基の薄層を膜の一方の面に形成する場合が多く、これは数ミクロンの厚みで充分な機能を発揮する。

このような薄層を酸化・還元反応その他の反応によって形成させたり、弱酸性の陽イオン交換基を有する薄いフィルムを強酸性の陽イオン交換膜の上に接着したりして形成した層が破壊される場合がある。従って、望ましくはこのような弱酸性の陽イオン交換基の薄層を化学反応

(14)

によって形成する場合、この化学反応の前に膜表面部の削除を実施すべきである。

以下の実施例によって本発明の内容を具体的に説明するが、以下の実施例によって本発明は何ら拘束されるものではない。

実施例 1

テトラフルオロエチレンとパーフルオロ〔3,6-ジオキサ-4-メチル-7-オクテンスルホンフルオライド〕からなる共重合体のTダイ押し出しシートを加水分解して、交換容量が0.91ミリ当量/グラム乾燥膜（B型）の厚みが178ミクロンの膜を得た（膜Aとする）。これを両面約5ミクロンづつ膜面に垂直に鋭利な刃を当てて削った。膜の厚みはマイクロメーターで測定したところ168ミクロンとなっていた（膜Bとする）。膜Aを同様に片面だけを約10ミクロン削った（膜Cとする）。また膜Aを特開昭53-58493号明細書に記載の方法で五塩化リンによりスルホン酸のスルホンクロライド化及びスルホンクロライド基のフ

(15)

ルコール中での空気酸化によりカルボン酸基への変換を行ない、残余のスルホンクロライド基を加水分解によりスルホン酸ソーダにし、イオン交換基として表層にカルボキシル基を持ち内部がスルホン酸基よりなる2重構造のイオン交換膜とする（膜Dとする）。

また別に膜Bを用いて上記処理を行なってイオン交換膜を得た（膜Eとする）。

更に膜Cの削除面を上記処理を行って別のイオン交換膜を得た（膜Fとする）。同様に膜Dのスムーズな面に対して上記処理を行なって得た膜をG膜とする。

これらの膜を用い食塩水溶液の電気分解を行った。即ち有効遊電面積1dm²、陽極チタニウム上に酸化ルテニウムコーティング、陰極鉄ラシよりなる電解槽により電流密度30A/dm²、80℃で陽極室の食塩濃度を3.5Nとし、陰極室から9Nの苛性ソーダを定常的に取り出した。いずれの膜においても電流効率はほぼ95%で苛性ソーダ中の食塩の量はほぼ60ppm（50

(16)

%苛性ソーダ換算）であった。膜の電気抵抗及び電解電圧を表1に示す。

表 1

	電気抵抗 (Ω -cm)	膜 厚 (ミクロン)	比抵抗 (Ω -cm)	電解電圧 (V)
スルホン酸型の膜				
削除前 (A膜)	0.56	178	31.5	—
両面5ミクロンづつ削除 (B膜)	0.42	168	25.0	—
片面10ミクロン削除 (C膜)	0.49	168	29.2	—
カルボン酸層形成の膜				
A膜をカルボン酸化処理 (D膜)	1.04	178	59	3.28
B膜をカルボン酸化処理 (E膜)	0.85	168	51	3.03
C膜の削除面をカルボン酸化処理 (F膜)	0.92	168	55	3.20
D膜の非削除面をカルボン酸化処理 (G膜)	0.88	168	52	3.13

実施例 2

テトラフルオロエチレンと $\text{CF}_2=\text{CF}-\text{O}-(\text{CF}_2)_5-\text{O}-\text{O}-\text{CF}_2$ の共重合体を押し出し成型によって厚み170ミクロンのフィルムとした。

(17)

このフィルムの交換容量は1.45ミリ当量/グラム乾燥膜であった。これを10%の水メタノールの1:1の混合溶液に50℃で16時間浸漬してカルボン酸基を有する陽イオン交換膜とした。この膜について、陽極側及び陰極側及び両面を約5ミクロンづつサンドペーパー（水研工業製AA400）で夫々削除し、3種類の膜を得た。膜の厚みはマイクロメーターによって測定した。これらの膜の電気化学的性質及びこれを用いて食塩電解を実施した。結果を表2に示す。

尚、陰極室からは35%の苛性ソーダを取得した他は実施例1と同様である。

表 2

	電気抵抗 (Ω -cm)	膜 厚 (ミクロン)	比電気抵抗 (Ω -cm)	電解電圧 (V)
表面削除処理前の膜	1.52	170	89.4	3.32
表面削除処理の膜 (両 面)	1.29	160	80.6	2.95
“ (陽極側)	1.32	160	—	3.05
“ (陰極側)	1.40	160	—	3.25

(18)

実施例 3

テトラフルオロエチレンと $\text{O}_2-\text{O}_2\text{O}-(\text{O}_2)_2-\text{SO}_2$ をアゾイソプロクロニトリルを触媒として共重合して高分子を得た。次いで、これを押し出し成型によって厚さ150ミクロンのフィルムとした。これをジメチルスルホキシド、水、水酸化カリウムの600:400:15の加水分解浴に浸漬してスルホニルフルオリド基をスルホン酸基に変換した。この変換容量は1.01ミリ当量/乾燥膜(H型)であった。この陽イオン交換膜の一方の面に5塩化リンの蒸気を接触させ、スルホン酸基をスルホニルクロライド基に変換し、次いでn-ブチルアルコール中で空気酸化してスルホン酸基に変換後、再び上記加水分解浴に浸漬して、一方の膜面に約10ミクロンのカルボン酸を有する膜とした。

ここで得られた膜の表層部を陽極側、陰極側両面について夫々サンドペーパー(三協理科学製006000W)で研磨により、表層を約5ミクロン削除した。これらの膜の性質及び食塩

(19)

ルホン酸ナトリウム基とした。これを更にH酸型に変えるために、1規定の塩酸中に室温下に15時間浸漬した。その後、水洗し、減圧乾燥して酸型のシートとした。

さらにスルホン酸基をカルボン酸基に変えるために、円筒状のガラス製反応器(内径10cm)の内壁に酸型のシートを削った面を外側にして取付け、反応器の中心部に東芝製殺菌ランプ(0L-15)をシートの表面からほぼ等距離となるようにセットした。反応器をオイルバスに浸漬し、150℃に加温した。又反応器の中を充分窒素で置換した後、真空ポンプで排気した。その後ポンプから一酸化窒素を1 $\mu\text{g}/\text{cm}^2$ 導入し、反応器を密閉し、殺菌ランプを点灯、30分間照射した。その後ランプを消し、反応器内に窒素を導入して、一酸化窒素をバージした。

他方比較のため片面を削りとらなかったシートについても同じ条件で処理を行った。処理後のシートの赤外スペクトル(A. T. R法)を測定したところ光が照射された部分はいずれも

(21)

電解時の性能を測定した結果を表3に示す。尚陰極室からは35%の苛性ソーダを定常的に取得した。

表 3

	電気抵抗 ($\Omega\text{-cm}$)	膜 厚 ミクロン	比電気抵抗 ($\Omega\text{-cm}$)	電解電圧 (V)	電流効率 (%)
表面削除してない膜	1.1	150	73	3.30	96
陽極側を削除した膜	0.90	140	64	3.15	96
陰極側を削除した膜	0.95	140	68	3.21	92
両面を削除した膜	0.85	140	61	3.00	95

実施例 4

実施例1で用いたテトラフルオロエチレンとパーフルオロ(3,6-ジオキサー-4-メチル-7-オクテンスルホニルフルオリド)の共重合体よりなるシート(加水分解処理前)の片面を実施例1の方法で20ミクロン削りとった。その後、シートを10%のNaOHを含むメタノール中に室温下に10時間浸漬してシート中のスルホニルフルオリド基を加水分解して、ス

(20)

1780 cm^{-1} にカルボン酸基の吸収帯が認められ、又1060 cm^{-1} のスルホン酸基の吸収帯が殆ど認められなかった。一方反対面はいずれも1780 cm^{-1} の吸収帯は認められず、1060 cm^{-1} の吸収帯が強く認められた。

これらのシートを陽イオン交換膜電解テストに供するため、処理後のシートを10%のNaOHを含むメタノール中に室温下に2時間浸漬した。浸漬後水洗して実施例1の方法に従って食塩水の電解テストを行った。得られた結果を表4に示す。なお電解槽に組込む時はカルボン酸基が存在する面(光を照射した面)を陰極側に向けた。

表 4

	電解電圧(V)	電流効率
削除した膜	3.18	95
削除してない膜	3.25	95

(22)